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The present invention is an improvement brought to patent EP 0620 607 BI (RECUPYL SA) which relates to a hydrometallurgical process of treatment of used piles allowing the recovery of the elements which may undergo beneficiation.

In urban waste, the electric piles and batteries are recognized like sources of toxic products requiring a particular treatment. The recycling of the different batteries to lead and nickel-cadmium is carried out for a long time and led to the recycling of lead and reusable nickel notably in the foundries of the second fusion.

The treatment of the piles is more complex, owing to the fact that their composition and their form are very varied. Several processes were proposed.

EP-A-409792 describes a process of simultaneous production of dioxide of manganese and of zinc by electrolysis of the solution obtained while treating by a solvent acid containing of the acid will tétra fluoroboric, of made up such as manganese oxides or zinc, zinc halides or metallic zinc, this process which can be applied with the treatment of used piles having undergone a calcining at 550 C in inert atmosphere.

JP-60096734 describes a process of treatment for the recovery of elements which may undergo beneficiation with EMI 1.1

to start from used piles, in which the piles are initially crushed, then heated at 500 C and then subjected to an chloro-ammoniacal treatment, then calcined. These processes require however a step of calcining which makes the operations long and expensive. Generally the processes of thermal or pyrometallurgical treatment operate at temperatures ranging between 600 and 750 C to recover mercury. Temperatures of 1500 C are same signaled. These thermal processes, fixed on the quantitative recovery of mercury are called with becoming, in the long term, obsolete. Moreover the very complex composition of the batches of piles leads to problems of elaborate material quality. In particular ferromanganeses are polluted by copper. Finally the use of chlorides considerably limits the field of beneficiation exiting products.

The hydrometallurgical processes are more adapt with the treatment without transfer of pollution and an improved valorization of materials contained in the matrices of piles.

It is substantial to note that the majority components of the piles are manufactured by hydrometallurgical way (electrolysis of zinc and chemical or electrochemical preparation of the manganese dioxide). These ways evolve/move in acid medium and function since numerous years on an industrial scale on quantities being expressed of ten thousands of tons.

It is obvious that the way acid gives access any present impurity in the piles.

Alkaline dies are to be proscribed insofar as single zinc is soluble in alkaline medium. This solubility is however reaching for concentrations raised into reactive basic and at an upper temperature at 95 C.

The alkaline treatment makes it possible to reach zinc but leaves the almost intact cathodic mass in the measuring or the species of manganese of valence (II), the cadmium or nickel, indium, mercury mercury and hydroxides are far from soluble in basic medium.

Single a new attack acid reducing similar to that described in EP 0.620.607 BI (RECUPYL SA) would make it possible to reach the totality of the compounds.

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But this new attack, if it had been suddenly carried out following an alkaline process, would require quantities of reactive very substantial because of the need to neutralize the black mass, mouthful of reactive strongly basic (of soda for example).

This neutralization followed by a reducing dissolution acid to attack the compounds Bi and trivalent manganese is accompanied by production of large quantities of sodium salts whose elimination or valorization is already problematic in other fields of treatment of waste.

Present the improvement answers of a manner favourable with all these disadvantages and thanks to a process which meets a double need: - environmental protection without transfer of pollution, - recovery of elements which may undergo beneficiation starting from used piles, requiring step of calcining and applicable to a nonsorted mixture of piles having different compositions.

Different the driving modes direct either acid or basic without reduction of manganese oxides leave a mercury residue still charged.

The use of a device including/understanding an oscillator with ultrasound or sonotrode submerged in the engine, bearing allows the quoted disadvantages.

The use of ultrasounds during the reaction of leaching makes it possible to increase the rate of extraction of mercury thanks to the phenomena of micro cavitations and microscopic thermal effects generated by the ultrasonic wave.

Some is the acid used, the attack of the piles led, with a mixed manganese and zinc solution.

Single an electrolysis as described in EP 0620607 BI RECUPYL currently makes it possible to separate effectively between zinc and the manganese which is then obtained either in the form of manganese dioxide or in the form of manganese according to the configuration of the cell and pH of the solution's.

These installations require a high technicality and a consequent investment which is justified especially for substantial tonnages with the inlet.

In order to bearing with this disadvantage and to be able to propose a process implemented by means of an investment economically acceptable whatever the capacity installed, the present invention offer an alternative which consists of a separation between zinc and manganese and a valorization in the form of products of wide use.

By this technology, it is possible to answer the principle of proximity by allowing the emergence of installations of low capacity which remain however profitable by the exiting product beneficiation towards so established traditional markets.

Description of the improvement brought:

The process of treatment of used piles of the present invention is a process in which one subjects the used piles to a mechanical treatment in order to dislocate the envelopes of the piles, then with a magnetic sorting in order to separate the ferrous metals from the metals nonferrous Hg, mn,

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Zn, Cd and Ni, then one subjects the fraction removed from the ferrous metals to a washing in order to dissolve soluble salts.

The grinding is carried out in a mill with toothed discs, preferably cold under a draught enriched of cold nitrogen gas. The grinding causes the dislocation of the metallic envelope of the piles and the reduction of ferrous sheets to sizes compatible with the subsequent operations.

The load obtained after grinding passed on a screen of equal mesh to 3 Misters. The fraction composing the refusal is subjected to a first magnetic sorting by means of ferrite a magnetic magnet pulley to separate the ferrous fraction from the refusal. The second fraction of this refusal is composed then of paper and plastic. The fine portion (thus screening) is subjected to a second magnetic treatment on rare ground a magnetic magnet drum to recover the fine ferrous ones. The whole of the mechanical installation in depression and is connected to a system of treatment of gases and dust.

The fine inorganic loads obtained after magnetic separation and sifting contain non-ferrous oxides and metals as well as the electrolyte, mainly in the form of potash, of chloride zinc and ammonium.

The continuation of the operations described in the present invention can be indifferently carried out on a load coming of a grinding or on a load resulting from a thermal treatment from the piles.

To extract the electrolytes effectively, an operation of scrubbing proves to be required. This operation of scrubbing revêt a cardinal importance insofar as it allows: - to accelerate the dissolution of soluble salts, - to reveal the metallic fractions which are masked by oxides absorptive on the surface.

This operation can advantageously be carried out in an engine of attrition.

In this case energy required with the desorption of the fine particles is brought by an agitator to several blades and whose orientation allows the inversion of the current of the solid liquid solution in suspension or pulp. The association of the number of movable of agitation and the shape of the tank of reaction makes it possible to optimize the attrition. In our case an octagonal tank makes it possible to control the effectiveness of this operation.

The intensive friction of the particles between them according to a controlled turbulence makes it possible as well as possible to detach the finest fractions and the salts absorptive on the large particles. To optimize this friction of particle, it is required to adjust the concentration of the solution.

The solid/liquid report/ratio is judiciously selected to allow this suitable friction between the solid particles while offering a volume sufficiently to ensure the pre-dissolution of the soluble fractions.

After the operation of attrition, the load then is sufficiently diluted to complete the dissolution of salts, to put in suspension the very fine particles and to ensure a density of pulp adapt with an hydraulic classification. After filtration, one subjects the dense inorganic muds to a leaching by the sulfuric acid leading to the putting in solution of the components of the electrodes of the crushed piles. The reaction is enough exothermic and maintains a temperature adapt with the reactional process.

This step is characterized in that:

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- \* the attack is carried out by means of sulfuric acid concentrated with a sufficiently low pH to dissolve the majority of the metals composing the mixture of piles. This step relates to the divalent metals and reduced manganese and in divalent form.

- . In order to pass in solution manganese of valence III and IV, this dissolution acid is carried out in the presence of any reducing agent with respect to the manganese dioxide in the scale of the potentials of oxidation-reduction. This reducing is advantageously chooses among oxygenated water, the steel shot, the iron filings or ferrous iron sulphate. This operation makes it possible to recover the entirety of manganese implemented in the piles.

- 'the extraction of trapped mercury in the black mass and zinc in the form of amalgam is increased thanks to the action of one ultrasonic wave generated by a called probe " sonotrode " submerged in the bath of leaching.

After separation of the insoluble carbonaceous residues in acid medium, the clear solution is subjected to a treatment of purification which includes/understands:

EMI-4.1

- \* the elimination of composed of mercury carried out: . in a first mode of application by a reactive selective collector of this metal which is the 2, 5 dimercapto thia diazol. in a second mode of application by cementing to the zinc powder to ambient temperature.

- \* the elimination of the metals electropositive than zinc (notably copper, nickel, lead, cadmium and indium) carried out by hot cementing by means of zinc powder the mixed sulphate solution thus obtained is neutralized by means of carbonate ammoniac in the presence of ammonia. The concentrations of the compounds are in stoichiometric relationship to the initial contents ions present zinc and manganese in the solution.

The capacity complexing of the ions ammoniac makes it possible to mask the zinc which remains in solution and to precipitate manganese in the form of carbonate.

The manganese carbonate is filtered, rinsed and dried. The control of its purity by analysis and diffraction of x-rays (figure 1) watch which the phase is pure and which it does not have there contamination by manganese sulphate, zinc sulphate or manganese oxides of upper valences (which tend to be formed during drying). Chemical precipitation allowed the production of mono manganese carbonate disperses with an enough homogeneous granulometry and the relatively spherical shapes of grains as shown in the figure 2.

In another mode of valorization, the manganese carbonate is put in contact with the appropriate acid to produce corresponding salt.

An example of application without that being exhaustive, consists in dissolving manganese carbonate by means of sulfuric acid to produce manganese sulphate in solution.

In addition to the traditional applications of this sulphate, it is used also as starting solution for manganese the electrochemical dioxide obtaining of structure adapt with its cathodic use as materials in the saline and alkaline piles. The product obtained by anodic oxidation of the solution of  $MnSO_4$  under 20 mA/cm<sup>2</sup> and at 90 °C perfectly indexes like a standard dioxide nesutite  $\gamma MnO_2$  (figure 3).

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In another mode of putting in work of the present invention, the zinc solution is subjected to a sufficient heating to allow the release of the gaseous ammonia which is recovered and re-used in the process. Remaining zinc in the form of a pure salt because free of manganese and heavy metals.

A mode of putting in work of the present invention which relates to the zinc solution consists in neutralizing the present solution by means of carbonic gas. This sparging until pH 7,3 conduit with the formation of a zinc carbonate precipitate in the composition is that of a hydrozincite (figure 4).

A thermal treatment of the hydrozincite leads to the formation of a white, pure and perfectly crystallized zinc oxide like the watch its spectrum of diffraction to x-rays deferred on figure 5.

CLAIMS 1. Proceeded of processing of used electric piles for the recovery of the elements which may undergo beneficiation, characterized in that the fraction resulting from a magnetic grinding after separation of the metallic fractions or from an unspecified thermal treatment is subjected to: \* an alkaline washing in order to eliminate

soluble salts by an operation from attrition, \* a leaching by the sulfuric acid assisted by one wave ultra sound in the presence of a reducing agent.

\* a separate purification of mercury in solution \* an elimination of the other heavy metals a separation between the zinc and the manganese which are recovered in the form of basic or neutral salts.

2. Process, according to claim 1, characterized in that the reducing agent is advantageously selected among oxygenated water or the compounds containing iron as the steel shot, the filings of iron or the sulphate ferrous.

3. Process, according to claim 1, characterized in that the mercury is recovered of a selective manner in acid medium and independently of the other metals, by means of the 2,5 dimercapto thiadiazole or of zinc powder at ambient temperature.

4. Process, according to claim 1, characterized in that the other heavy metals are separated by an operation from hot cementing by means of zinc powder.

5. Process, according to claim 1, characterized in that the solution resulting from leaching acid and the two steps of purification is treated by means of an ammonia and ammonium carbonate mixture.

6. Process, according to claims 1 to 5, characterized in that the manganese is separate in the form of manganese carbonate having a low zinc content and free of other salts or manganese oxides.

7. Process, according to claims 7, characterized in that zinc is separate in the form of a soluble zinc ammonia complex having a very low manganese content.

8. Process, according to claim 1 to 5, characterized in that the soluble zinc ammonia complex is subjected to a sufficient heating to allow the departure of gaseous ammonia and leaving a salt of pure zinc.

9. Process, according to claim 7, characterized in that the soluble zinc ammonia complex is subjected to a neutralization by means of carbonic gas to precipitate zinc in the form of hydrozincite.

10. Proceeded according to claim 6 characterized in that the manganese carbonate obtained is put in solution by means of sulfuric acid in order to be used in the state.

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11. Proceeded according to claim 10 characterized in that the manganese sulphate is converted by standard manganese dioxide anodic oxidation  $\gamma\text{-MnO}_2$  by means of an electrolysis.